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Research paper

Alloying of metal nanoparticles by ion-beam induced sputtering

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ABSTRACT

Ion-beam sputtering technique has been utilized for controlled synthesis of metal alloy nanoparticles of compositions that can be tuned. Analysis of various experimental results reveals the formation of Ag-Cu alloy nanoparticles on a silica substrate. Surface-plasmon optical resonance positions and observed shifts of Ag Bragg angles in X-ray diffraction pattern particularly confirm formation of alloy nanoparticles on glass samples. Sputtering induced nano-alloying mechanism has been discussed and compared with thermal mixing of Ag and Cu thin films on glass substrates. Compositions and sizes of alloy nanoparticles formed during ion-beam induced sputtering are found to exceed far from the values of thermal mixing.

1. Introduction

The synthesis of bimetallic particles has attracted much interest due to their excellent chemical, optical, catalytic and magnetic properties, with many other applications [1–6]. There are many reports on the synthesis of alloy particles made from miscible metals, but the studies on alloy particles with bulk immiscible or poorly miscible systems like Ag-Cu are limited [7–9]. Synthesizing alloy nanoparticles beyond the miscibility range is particularly important due to their interesting physical properties that cannot be achieved in phase segregated mixtures [5].

Optical properties of nanoscale metal/alloy particles have attracted much interest in recent times [10]. As the linear and non-linear optical properties of nanoparticles are dependent on the frequency at which the surface-plasmon resonance (SPR) occurs, studies related to tune the SPR frequency is of great importance [11]. Through the formation, and controlling sizes and compositions of alloy metal nanoparticles, optical responses of such nanomaterials may be tuned in the UV-Visible ranges of light for various optoelectronic applications. There are only a few reports on bimetallic Ag-Cu alloy particles [8–10]. Large difference in lattice parameter of Cu and Ag makes the synthesis of Ag-Cu alloy difficult through equilibrium processes [12]. In contrary, ion beam irradiation is a non-equilibrium process and hence thermodynamic solubility limit of various immiscible systems can easily be overcome leading to the nucleation and growth of the metal alloy nanoparticles [13,14].

In the process of sputtering by ions with energy (hundred to a few hundreds of keV), the sputtered metal atoms may come out with energy in the range of few hundreds of eV [15]. These sputtered atoms impinging the surface of a substrate transmit energy among the surrounding atoms and this may result in local heating. When substrate is insulator, this heat is localized in a small zone (of the order of a few nm) and may induce a thermal spike [16]. Spiked temperature in the confined region may result in melting and intermixing of atoms on the substrate regardless of their thermodynamic properties [17]. This whole process of thermal spike may result in the formation of a metastable phase and this phase may quench in a few picoseconds [17,18]. Also, advantage of this technique is that the synthesis occurs in a high vacuum atmosphere. Thus, metals like Cu can form alloy phases with other immiscible metals without being oxidized. It may be difficult to achieve such pure phases with liquid chemical processes and pulsed laser assisted alloying methods [7]. Here, we report a controlled method of synthesis of Ag-Cu alloy nanoparticles with varying composition beyond miscibility limit on a silica-glass substrate by the Ar^+ ion beam induced sputtering technique. In this composite material the SPR frequency can be tailored in the range from the SPR frequency of pure Ag to that of pure Cu.

2. Experimental details

Ion-beam sputtering (IBS) technique has been utilized for the synthesis of the alloy nanoparticles [19]. More of the experimental

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details are available elsewhere [20]. A small copper (Cu) foil of 0.5 mm thickness was placed at the centre of a silver (Ag) foil ($16 \times 12 \times 0.5$ mm). These foils were irradiated by 100 keV Ar^+ ion beam with a fixed ion dose of 1×10^{17} ions cm^{-2} at normal incidence. The sputtered Ag and Cu atoms were collected on a silica-glass substrate kept at an angle of 45° with respect to the target foils. The amount of Cu and Ag atoms sputtered has been controlled by varying the area of the Cu foil only. Depending on the area of Cu targets, samples prepared are named as 'L', 'M', and 'S' for Cu foils of sizes 7×7, 5×5 and 3×3 mm, respectively. This notation has been followed throughout the manuscript. Scanned ion-beams on the target over an area ~1 cm^2 were used to achieve required sputtering in a high vacuum chamber (~10^{-7} mbar). Ar^+ ion irradiation was carried out using the 150 kV particle accelerator at IGCAR, Kalpakkam. UV–Visible optical absorption measurements were recorded in the wavelength range of 200–800 nm using Aventes spectrophotometer. Planar electron transparent specimens were examined using a LIBRA 200 Zeiss HRTEM. Glancing incidence X-ray diffraction (GIXRD) measurements were carried out using Inel Equinox 2000 diffractometer. The angle of incidence during GIXRD measurements was kept at 0.5°. The measurement resolution of the X-ray diffraction system is 0.03°. For thermal mixing studies, Ag (70 nm)/Cu (70 nm) thin films were deposited on silica-glass glass substrates using a vacuum thermal evaporator system. The base pressure of the chamber was ~10^{-6} mbar during deposition. Thermal annealing of these samples was carried out in vacuum (~10^{-6} mbar) at 400 °C up to 2 h for the mixing to occur. The elemental composition of the thermally mixed and sputter deposited Ag/Cu samples on a-SiO_2 substrates were measured by Rutherford backscattering spectrometry (RBS). He^+ ions of energy 2 MeV from 1.7 MV Tandetron accelerator (HVEE, The Netherlands) was used for the RBS measurements. Surface barrier solid state detector at scattering angle of 165° was employed for the detection of the backscattered He^+ ions.

3. Results and discussions

Glancing incidence X-ray diffraction (GIXRD) patterns of the ion-beam sputter (IBS) deposited and thermally annealed samples have shown corresponding diffraction peaks belonging to pure Cu and Ag metals. In both class of samples, sputter deposited and thermally annealed, effect of alloying has resulted in small shifts of the X-ray diffraction peaks with respect to corresponding diffraction peaks of pure metals. Changes of the lattice parameters due to the nano-alloying have been calculated from the observed shifts of the X-ray diffraction peaks. Formation of the nano-alloy has been further elucidated in subsequent discussions taking clues from optical absorption and electron microscopy studies.

3.1. IBS samples

GIXRD patterns of the IBS deposited samples are shown in Fig. 1. Bragg diffraction peaks corresponding to Ag gradually shift towards higher 2θ values for samples with higher concentration of Cu atoms. The diffraction peaks corresponding to Cu marginally shift towards lower 2θ values for samples with higher concentration of Cu atoms (as shown in Fig. 1). Alloy nanoparticles samples named as 'S' and 'L' have the lowest and the highest concentration of Cu atoms, respectively. During the process of alloying, smaller Cu atoms (Cu atom is smaller than Ag by 12%; lattice constant differs by ~14%) may replace a fraction of Ag atoms in the crystalline lattice structure of Ag. As a result, lattice contraction of Ag may take place. With the shrinking of lattice spacing, Bragg's law

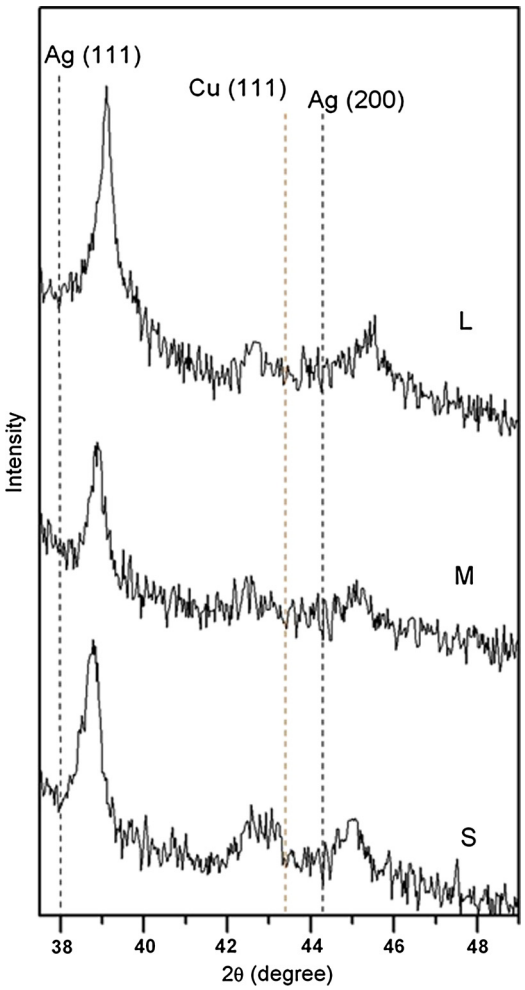

Fig. 1. GIXRD patterns of IBS deposited Ag/Cu on silica-glass substrates. Black dashed lines correspond to the diffraction peaks of Ag (1 1 1), Ag (2 0 0) and the orange line shows Cu (1 1 1) diffraction peak in as deposited Ag/Cu bilayer samples on silica-glass substrates. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

enforces the Ag diffraction peaks to shift to higher 2θ values and Cu diffraction peaks to shift to lower 2θ values. However, only marginal shifts were observed in the Cu peak positions. This may be due to formation of pure Cu nanoparticles along with alloy nanoparticles. Since the total intensity and the shift of Cu peaks are small, it is difficult to distinguish between diffraction signals of pure Cu nanoparticles and the alloy nanoparticles. As shown in Table 1, for samples S, M and L, Ag (1 1 1) X-ray diffraction peak positions have been observed at 38.8°, 38.9° and 39.1°, respectively. For as coated Ag/Cu bilayer sample Ag (1 1 1) peak is at 38.0°. This shift has been used to determine alloy composition using Vegard's law [9] (Ag (1 1 1) & Ag (2 0 0) peaks have been used for calculation (to best of our knowledge, experimental data regarding lattice parameters for various compositions of Ag-Cu alloy is not currently available). X-ray diffraction data for the as-coated Ag/Cu film has been taken as the reference for estimation of peak shifts. Average volume% of Cu in the alloy nanoparticles in samples S, M and L are 14, 16 and 23%, respectively. These values are in agreement with the available experimental data for Ag-Cu metastable solid solution [21]. The volume% of Cu is found to be more than previously reported values as well as more than the maximum thermal equilibrium concentration (13.5 vol.%) [8,9,22].

Debye-Scherer's formula (Eq. (1)) has been used to calculate sizes (R) of the alloy nanoparticles,